

Electrodeposition of nanocrystalline copper thin films from 1-ethyl-3-methylimidazolium ethylsulphate ionic liquid

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Abstract Copper thin films are increasingly important as interconnectors for the creation of smaller and better performing integrated circuits and electrodeposition from ionic liquid-based electrolytes could provide a greener fabrication method for these films. The electrodeposition of copper from copper(I) and copper(II) salt solutions in a low cost, widely available ionic liquid, 1-ethyl-3-methylimidazolium ethylsulphate, was studied using a range of different deposition potentials and temperatures. Three different electrolytes containing ~0.1 M of copper(I) chloride (CuCl), copper(II) chloride (CuCl₂) and copper(II) sulphate (CuSO₄) were used. Under similar deposition conditions, the films obtained from CuCl and CuSO₄-based electrolytes presented better continuity than films obtained from CuCl₂-based electrolyte. Continuous films with a homogeneous structure were obtained by electrodeposition from CuCl and CuSO₄-based solutions at a constant potential of

–1.8 V and a temperature of 35 °C. Under similar deposition parameters, the films deposited from CuCl₂-based electrolyte presented the largest particle size, while those deposited from copper(I) chloride and CuSO₄-based solutions presented finer microstructures. X-ray diffraction analysis and energy dispersive X-ray spectroscopy showed that the deposits were crystalline and consisted mainly of copper, with traces of oxygen and sulphur resulting from residues of the ionic liquid. The films presented a nanocrystalline microstructure consisting of particles about 25 nm, aggregated in clusters.

Keywords Electrodeposition · Ionic liquid · EMIM-EtSO₄ · Copper · CuCl · CuCl₂

1 Introduction

Electrodeposition is an important industrial process. An example is the deposition of copper thin films, which are widely used in the electronics industry, such as the creation of copper-based interconnects in integrated circuits [1, 2] and in the packaging of copper-based interconnects in 3D integrated devices [3]. The electrolytes used in copper electrodeposition are usually water-based, but aqueous solutions present important drawbacks as electrodeposition media, in particular low cathodic deposition current efficiency due to simultaneous water decomposition [4] and a tendency for the films to present poor mechanical properties due to hydrogen embrittlement [4]. Moreover, many industrial aqueous electrolytes present unacceptable health and environmental impacts [5].

The quest to reduce the health and environmental impacts of the electrodeposition process generated an increasing interest in ionic liquids-based electrolytes. Ionic

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liquids present low vapour pressure, and are non-toxic and non-flammable, thus reducing the impact of these processes [6]. Moreover, pure ionic liquids are chemically stable and present large electrochemical windows, allowing the deposition of high quality films of a wide range of materials, including films of reactive metals which cannot be deposited from aqueous solutions [4]. Their main drawback is a high cost, but even so, the process is still cheaper than other high quality thin film deposition methods, such as sputtering and chemical vapour deposition [4].

Several studies on copper electrodeposition from ionic liquid solutions have been reported in the literature. The electrochemical behaviour of Cu(I) solutions in 1-ethyl-3-methyl imidazolium tetrafluoroborate (EMIM-BF₄) was studied by Chen and Sun [7]. The authors showed that the Cu(I) ions in (EMIM-BF₄)-copper(I) chloride solutions can be oxidised to Cu(II) or reduced to metallic copper in appropriate conditions and fairly dense copper films can be electrodeposited from these solutions. The required potential depended on the substrate material: underpotential deposition occurred for platinum, but an overpotential was required to initiate deposition on glassy carbon. Murase et al. [8] studied the redox behaviour of Cu(I) and Cu(II) salt solutions in trimethyl-*n*-hexylammonium bis((trifluoromethyl)sulfonyl)amide (TMHA-Tf₂N) to evaluate the applicability of this ionic liquid in copper deposition and concluded that copper thin films can be produced from Cu(I) salt solutions. The process involves a single-electron reduction reaction and presents a current efficiency of almost 100 %.

El Abedin et al. [9] showed that the solubility of Cu salts in 1-butyl-1-methylpyrrolidinium bis((trifluoromethyl)sulfonyl)amide (BMP-Tf₂N)-based electrolytes is limited. However, they succeeded in introducing Cu(I) ions in solution by anodic dissolution of copper and deposited copper thin films on gold substrates by an appropriate variation of the applied potential. The films presented a nanocrystalline structure with an average particle size of 50 nm.

Some ionic liquids present higher solubility for copper salts. Leong et al. [10] showed that the solubility of CuCl and CuCl₂ in 1-ethyl-3-methylimidazolium dicyanamide (EMIM-DCA) are 1.1 and 0.9 M, respectively, making them attractive electrolytes for copper deposition. Moreover, the viscosity of EMIM-DCA is lower than the viscosities of other similar ionic liquids, improving the mass transport and electrodeposition kinetics. The authors showed that continuous nanocrystalline copper films can be obtained at low overpotential by electrolysis of the CuCl/EMIM-DCA solution. The films formed by a three-dimensional progressive nucleation and growth process. On the other hand, Brooks et al. [11] achieved high copper electrodeposition rate by using specially designed ionic

liquids containing the metal cation. The authors deposited copper at current densities greater than 25 A dm⁻² from an ionic liquid containing Cu(I) and the Tf₂N anion ([Cu(CH₃CN)_{*n*}]-Tf₂N), *n* = 2, 4), thus overcoming the solubility and mass transport limitations found in previous work. Abbot et al. [12] successfully deposited copper and copper composites from 0.1 M CuCl₂ 2H₂O in an ionic liquid consisting of choline chloride and hydrogen bond donors such as urea or ethylene glycol.

These ionic liquids are in general, too expensive for practical application. The present work aims to investigate the deposition of copper thin films from an electrolyte based on an inexpensive, environment-friendly and widely available ionic liquid. Based on the above criteria, as well as its promising physical and chemical properties [13, 14], 1-ethyl-3-methylimidazolium ethylsulphate (EMIM-EtSO₄) was chosen as the solvent for electrodeposition.

2 Experimental methods

The electrolytes used in the present work were prepared by dissolving copper(I) chloride (CuCl), copper(II) chloride (CuCl₂ 2H₂O) and copper(II) sulphate (CuSO₄ 5H₂O) in 1-ethyl-3-methylimidazolium ethylsulphate (EMIM-EtSO₄, for synthesis, Merck). The nominal solute concentrations for the three salts were 0.1 M, but while CuCl₂ dissolved in the ionic liquid up to this concentration, a small amount of undissolved salt remained in 0.1 M CuCl and CuSO₄ solutions, resulting in real solute concentrations slightly lower than the nominal ones. In order to reduce the water content of the electrolyte, the salts were dried in an oven at 100 °C for at least 72 h before preparing the solutions in a glove box (MBraun-UNilab systems TP170b mono) containing an argon atmosphere with O₂ and H₂O contents below 0.1 ppm. To ensure the dissolution of the salts and the homogenisation of the solutions, the mixtures were heated at 35 °C for 72 h with permanent stirring.

The electrochemical experiments were carried out inside the glovebox, using an AutoLAB PGSTAT100 potentiostat with Nova 1.5 software and a three-electrode configuration 10 mL electrochemical cell. The working electrode was a glassy carbon disc, with an area of 0.071 cm² and the counter electrode a platinum foil, with an area of 1.0 cm². A platinum wire was used as a quasi-reference electrode (QRE). Cyclic voltammograms were recorded by first sweeping the potential in the cathodic direction from the open-circuit potential to -2.0 V and then in the anodic direction up to +1.0 V and back to the starting potential. The potential scan rate was 50 mV s⁻¹. The chronoamperometry experiments were performed by applying a constant potential to the electrodes while measuring the current over a 30-s period.

Electrodeposition experiments were performed by varying three parameters, the deposition potential chosen between -0.1 and -1.8 V versus a Pt QRE; the deposition time fixed at 900 and 1,800 s; and the electrolyte temperature fixed at 35, 50 and 85 °C. The substrates were nickel plates (99.98 %, Goodfellow) with an exposed area of about 0.25 cm^2 . The electrolyte was stirred during deposition. After deposition, the substrates were removed from the electrolyte and left to cool down to room temperature before rinsing off the remaining electrolyte with acetone and blow-drying.

The structure of the films was characterised by scanning electron microscopy (SEM) using a JEOL model JSM-7001F field emission gun SEM equipped with energy dispersive X-ray spectroscopy (EDX). The films crystallographic structure was analysed by glancing incidence X-ray diffraction (GI-XRD) using a Siemens D5000 diffractometer and Cu $K\alpha$ radiation. The experiments were carried out with an incidence angle of 1° and a 2θ range between 40 and 80° . The peaks observed in the diffractograms were indexed by comparison with JCPDS database files. The film crystallite size was estimated from the diffraction peaks broadening using Scherrer's equation [15]:

$$t = \frac{0.9\lambda}{B \cos \theta}$$

where λ is the X-rays wavelength in nanometres, B the peak broadening and θ the Bragg angle, both in radians. Transmission electron microscopy (TEM) observations were carried out with a Hitachi H8100 LaB₆ gun 200 kV microscope. The TEM specimens were obtained by detaching fragments of the films from the substrate with a scalpel and depositing these fragments on formvar-coated 200-mesh copper grids.

3 Results and discussion

The cyclic voltammogram of EMIM-EtSO₄ at 35 °C obtained with a glassy carbon electrode is depicted in Fig. 1a. Following the definition of electrochemical stability window that the current density does not exceed 0.001 A cm^{-2} , a stability window of 4 V (between -2.5 and $+1.5$ V) was found for this ionic liquid, in agreement with the literature [16, 17]. The sudden increase in the cathodic current at -2.1 V during the forward scan was due to the reduction of the [EMIM]⁺ cation [16]. In the reverse scan an anodic peak is observed at -0.6 V, corresponding to the oxidation of the species formed in the forward scan.

The cyclic voltammograms of the CuCl, CuCl₂ and CuSO₄ solutions in EMIM-EtSO₄ at 35 °C are presented in Fig. 1b–d. When compared to the voltammogram of the

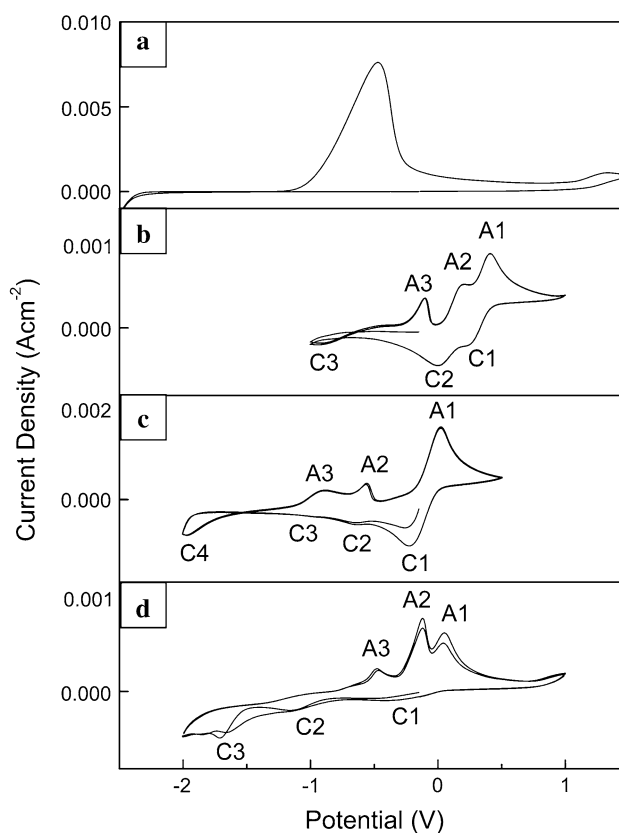


Fig. 1 Cyclic voltammograms of **a** pure solvent, **b** 0.1 M CuCl, **c** 0.1 M CuCl₂ and **d** 0.1 M CuSO₄ solutions in EMIM-EtSO₄, at 35 °C. The working electrode was a GC disc and the scan rate 50 mV s^{-1}

pure ionic liquid (Fig. 1a), the presence of the Cu ions in solution gives rise to several new peaks.

The voltammogram of the 0.1 M CuCl solution (Fig. 1b) presents a cathodic peak at -0.95 V (C3), which can be attributed to the reduction of Cu(I) to metallic copper, in agreement with previous authors [7, 8, 10]. Two other cathodic peaks appear at 0.24 V (C1) and -0.00 V (C2). The potential of peak C2 is characteristic of the reduction of Cu(II) to Cu(I) [7, 8, 10], suggesting that Cu(II) was present in the CuCl solution. The presence of Cu(II) in a CuCl solution can be explained by the occurrence of a disproportionation reaction leading to the oxidation of Cu(I) to Cu(II) or by the presence of the divalent cation in the original CuCl salt as an impurity, as suggested by the pale green colour of the electrolyte. In the reverse scan, a nucleation loop with a crossover at -0.69 V, corresponding to the nucleation of metallic copper on the substrate [18]. The reverse scan presents a further three peaks, the first one at -0.1 V (A3), corresponding to the oxidation of the metallic copper formed during the forward scan to Cu(I), the second one, at 0.18 V (A2), to the peak at C1 and the third one, at 0.41 V (A1), to the oxidation of Cu(I)–Cu(II).

The voltammogram of the 0.1 M CuCl_2 solution (Fig. 1c) presents a cathodic peak at -0.30 V (C1), due to the reduction of $\text{Cu(II)}\text{--Cu(I)}$ and two cathodic peaks C2 and C3 at -0.73 and -1.06 V, respectively, which are probably associated to the presence of impurities in the electrolyte, in particular water [8]. The peak at -1.9 V (C4) can be ascribed to the reduction of Cu(I) to metallic copper. Similar to the CuCl solution, the reverse scan presents a nucleation loop with a crossover at -1.59 V, corresponding to the nucleation of metallic copper on the substrate [18]. The anodic peaks at -0.92 (A3) and -0.55 V (A2) may be attributed to the oxidation of the metallic copper formed to Cu(I) and the peak at 0.02 V (A1) to the oxidation of $\text{Cu(I)}\text{--Cu(II)}$.

In the voltammogram of the CuSO_4 solution (Fig. 1d), a cathodic wave at -0.67 V (C1) indicates the reduction of $\text{Cu(II)}\text{--Cu(I)}$. The cathodic peak at -1.25 V (C2) is probably associated to the presence of impurities in the electrolyte, such as water [8], while the peak at -1.68 V (C3) can be ascribed to the reduction of Cu(I) to metallic copper. In the reverse scan, the anodic peaks at -0.47 V (A3) and -0.12 V (A2) are related to the oxidation of metallic copper to Cu(I) and the anodic peak at 0.05 V (A1) is related to the oxidation of $\text{Cu(I)}\text{--Cu(II)}$, respectively.

The cyclic voltammograms of both the CuCl and CuCl_2 solutions appear to have a similar shape, which is expected as they both contain similar ions in solution. However, one major difference is that all the peaks in the CuCl_2 solution appear at more negative potentials when compared to the CuCl solution. A possible reason for this is that the metal complex of copper ions in CuCl and CuCl_2 may be different, and it is easier to reduce the copper from metal complex from the CuCl solution compared to the CuCl_2 solution. For the EMIM- EtSO_4 ionic liquid, the less negative potential of the cathodic peak corresponding to the reduction of Cu(I) to metallic copper appears to make the CuCl solution a better electrolyte choice. This is because a high nucleation potential will be required to form a smooth, compact and uniform film as will be shown in the following paragraphs.

The stability of the CuCl , CuCl_2 and CuSO_4 solutions decreases with an increase in deposition temperature. As the deposition temperature is increased, the cathodic and anodic peaks shift to a more positive potential. An example of this can be seen for the CuCl_2 solution (Fig. 2), where the C4 reduction peaks shift from -1.9 V at 35°C , -1.8 V at 50°C and finally -1.6 V at 85°C . Besides the shift in peak potentials, there was an increased in the overall current density of the cyclic voltammograms with increasing temperature. Changes were also observed in the relative current density values between the anodic and cathodic peaks in the cyclic voltammograms at different temperatures. At 35°C (Fig. 2a), the A1 oxidation peak has a much higher current density when compared to the A2 and A3

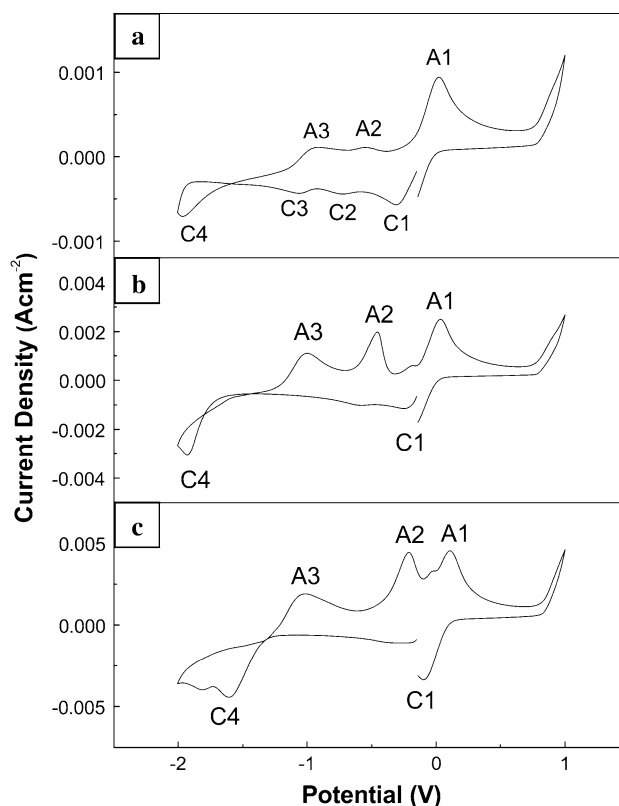


Fig. 2 Cyclic voltammograms of 0.1 M CuCl_2 solution in EMIM- EtSO_4 at **a** 35°C , **b** 50°C and **c** 85°C . The working electrode was a GC disc and the scan rate 50 mV s^{-1}

peaks. However at 50 and 85°C (Fig. 2b, c), the relative difference in the current densities of the A2 and A3 peaks in comparison with the A1 peaks were not as pronounced when compared with the same peaks at 35°C (Fig. 2a). There were no increased in the current densities of the C2 and C3 peaks with the increased in experimental temperature, with both peaks completely disappear from the cyclic voltammogram at 85°C . This supports the argument that the C2 and C3 peaks are due to the presence of impurities, with water as the likely candidate. At the experimental temperature of 50°C , a new oxidation peak appears at -0.3 V. This peak shifted to -0.1 V and has grown larger as the temperature was increased to 85°C . This new peak could be due to the formation of less stable oxidation product due to the increased in thermal energy. Changes in colour of the solutions were observed as the temperature was increased. The colour of the CuCl_2 and CuSO_4 solutions were dark green and green at 35°C but changes to light green and greenish blue at 85°C . The colour change may indicate a change in the ionic complex in the solution or the breakdown of the solvent component in the solution. There were no significant changes in the colour of the CuCl solution as it remains light green at all deposition temperatures.

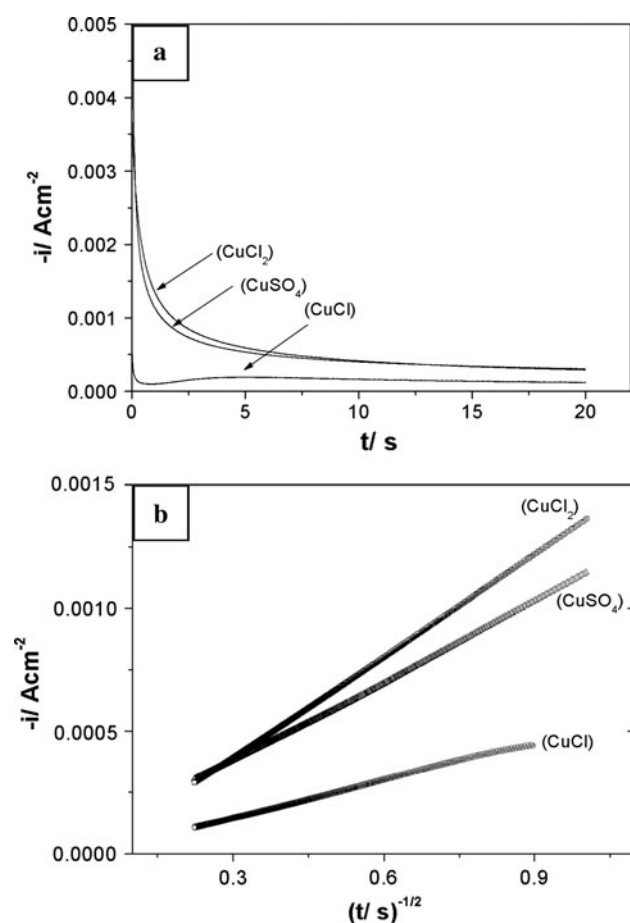


Fig. 3 **a** Chronoamperograms of 0.1 M CuCl, CuSO₄ and CuCl₂ obtained at 35 °C on a GC disc electrode with potential steps of −1.0, −0.7 and −0.3 V, respectively; and **b** respective variation of the current density with $t^{-1/2}$

These cyclic voltammetry results show that the reduction of Cu(II) solutions in EMIM-EtSO₄ occurs in two steps, independently of the Cu salt in solution and in agreement with the results reported for Cu(II) solutions in EMIM-DCA [10], EMIM-BF₄ [7] and TMHA-Tf₂N [8]. The results achieved also show that the range of potential for copper deposition for the three electrolytes lies between −1.5 and −2.0 V. The difference of potential between the peaks corresponding to the Cu(II)/Cu(I) and Cu(I)/Cu(0) redox reactions for the three solutions is large, but comparable to the values reported in the literature when glassy carbon is used as the working electrode material [7, 10].

Figure 3a presents chronoamperograms acquired for potential steps in the range corresponding to the reduction of Cu(II) (in CuCl₂ and CuSO₄ solutions) and Cu(I) (in CuCl solutions). After an initial current oscillation due to double-layer charging, the current density, i varies linearly with $t^{-1/2}$ (Fig. 3b), according to the Cottrell equation [19]:

$$i = \frac{nFD^{1/2}C_0}{(\pi t)^{1/2}}$$

The Cottrell equation is used to estimate the diffusion coefficient values from the slope of the i versus $t^{-1/2}$ plot. The diffusion coefficient values obtained are presented in Table 1. The diffusion coefficients increase with temperature as expected, but the values are about an order of magnitude smaller than those found for Cu(I) and Cu(II) salt solutions in EMIM-DCA (2.13×10^{-6} and 2.06×10^{-6} cm² s^{−1}, respectively [10]) and about half the values found for Cu(I) and Cu(II) salt solutions in EMIM-Cl-BF₄ (2.3×10^{-7} and 1.5×10^{-7} cm² s^{−1}, respectively [7]). This difference is due to the higher viscosity of EMIM-EtSO₄ [14] as compared to EMIM-DCA and EMIM-Cl-BF₄ [10] and suggests that these ionic liquids may allow higher deposition rate under similar deposition conditions.

Visible films were obtained from the CuCl₂ solution at an applied potential of −1.6 V. For each temperature, increasing the deposition potential from −1.6 to −1.8 V improves the continuity of the films without altering their microstructure. At a constant deposition potential, increasing the deposition temperature has a strong effect on the microstructure of the films, as shown by the SEM micrographs of films deposited at −1.8 V for 900 s from the CuCl₂ solutions (Fig. 4a–c). The films deposited at 35 and 50 °C (Fig. 4a, b) consist of globular particles with an average diameter of approximately 100 nm, but at a deposition temperature of 85 °C (Fig. 4c), the particles are polyhedral, with visible crystallographic facets and their size varies between 0.5 and 5 μm. This indicates that the nucleation rate is low and the growth rate is high, while the opposite occurs at lower temperature.

Visible films were obtained from the CuCl solution at an applied potential of −0.8 V. The films obtained were discontinuous, and increasing the deposition potential to −1.8 V significantly improves the continuity of the films. At a constant deposition potential, increasing the deposition temperature increases the film roughness, as shown by

Table 1 Diffusion coefficient of the copper species from the three salts in EMIM-EtSO₄ solutions calculated from chronoamperometry data

Solution	Diffusion coefficient, D (cm ² s ^{−1})		
	35 °C	50 °C	85 °C
0.1 M Cu(i)Cl–EMIM-EtSO ₄	1.78×10^{-07}	2.28×10^{-07}	2.05×10^{-06}
0.1 M Cu(ii)Cl ₂ –EMIM-EtSO ₄	5.70×10^{-08}	1.49×10^{-07}	2.92×10^{-06}
0.1 M Cu(ii)SO ₄ –EMIM-EtSO ₄	3.04×10^{-09}	8.44×10^{-09}	9.13×10^{-07}

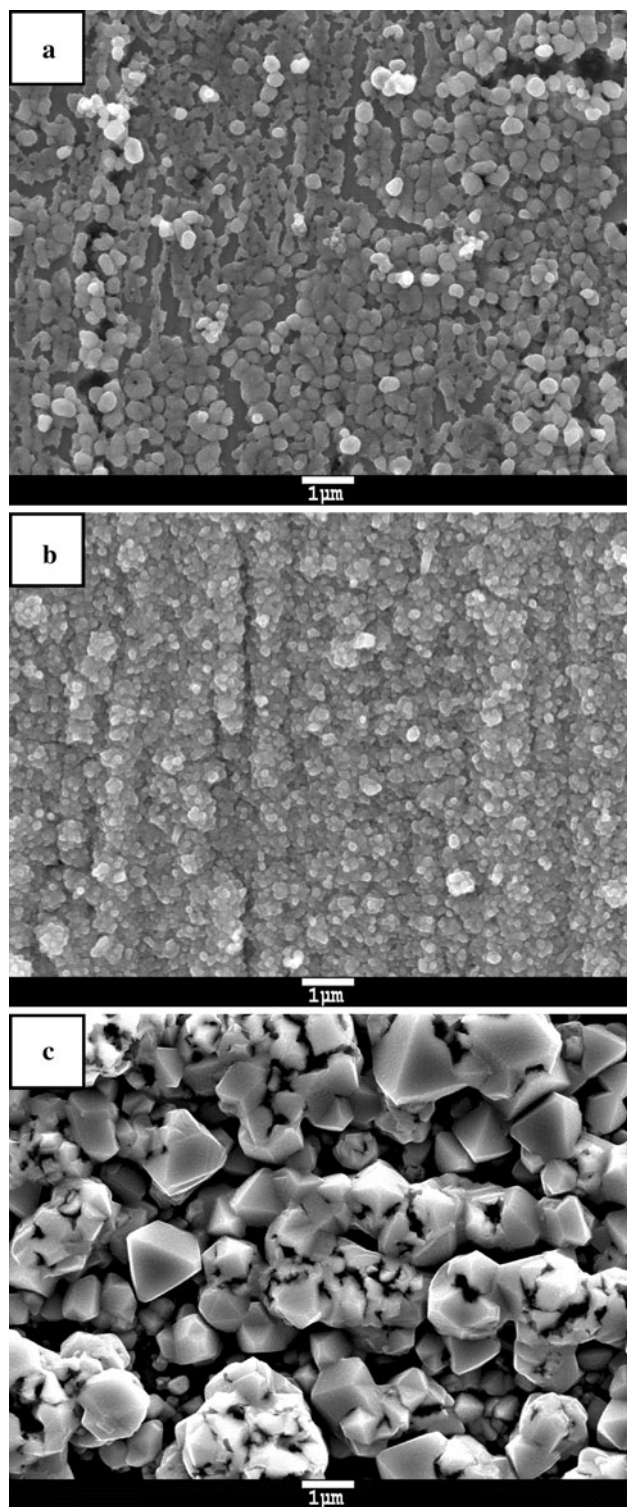


Fig. 4 SEM micrographs of films electrodeposited from 0.1 M CuCl_2 electrolyte at -1.8 V for 900 s at **a** 35, **b** 50 and **c** 85 °C

the SEM micrographs of the films deposited at -1.8 V for 900 s from the CuCl solution (Fig. 5a–c). The films deposited at 35 °C are continuous and regular, consisting of globular particles with an average particle size of

100 nm (Fig. 5a). As the deposition temperature is increased to 50 °C, the film roughness increase as globular clusters with a diameter of around 1 μm were formed (Fig. 5b). When deposition is carried out at 85 °C (Fig. 5c), the average particle size remains close to 100 nm, but larger irregular aggregates of these particles were formed, further increasing the roughness.

At most deposition temperatures, visible films were obtained from the CuSO_4 solution at an applied potential of -1.6 V. An exception is at the deposition temperature of 85 °C, where an almost continuous film which consists of globular particles with sizes ranging from 100 to 500 nm were obtained from an applied potential of -1.2 V. The abovementioned film presents some roughly circular pores, probably due to evolution of hydrogen resulting from the decomposition of H_2O present in the electrolyte as an impurity. As the deposition potential becomes more negative (from -1.2 to -1.8 V), the particle size decreases and the continuity of the films is improved. The changes in the microstructure of films deposited from the CuSO_4 electrolyte at -1.8 V with deposition temperature are shown in Fig. 6a–c. Continuous films consisting of sub-micrometric globular particles are obtained at 35 (Fig. 6a) and 50 °C (Fig. 6b). The average particle size increases from about 100 nm at 35 °C to 200 nm at 50 °C. At an electrolyte temperature of 85 °C (Fig. 6c), overgrowth occurs, similarly to what was observed for the CuCl electrolyte in the same conditions.

Comparing the films prepared from the different electrolytes (Figs. 4, 5, 6), it is clear that the films deposited from the CuCl_2 solution present a larger particle size and are less continuous than those deposited from CuCl and CuSO_4 solutions with similar deposition parameters. A possible explanation is that the nucleation of copper occurs at a much more negative potential in the CuCl_2 solution compared to the CuCl solution. From the cyclic voltammogram in Fig. 1, we can see that the nucleation loop corresponding to the deposition of metallic copper occurs at -0.69 V for the CuCl solution and at -1.59 V for the CuCl_2 solution, indicating that the potential required for copper nucleation is much lower for the CuCl solution compared to the CuCl_2 solution. Hence at deposition potential of -1.6 and -1.8 V, the number of nucleation for the CuCl_2 solution will be low as they can only form on the most ideal active site as the activation energy for nucleation is high. With a low number of nucleation, the grain size will be much larger as there are more room for the grains to grow. For the CuCl solution, there is a massive overpotential when copper was deposited at -1.6 and -1.8 V. With the higher overpotential, nucleation can form on the weaker active sites hence the number of nucleation for copper deposited from the CuCl solution will be much higher than the CuCl_2 solution. The higher nucleation

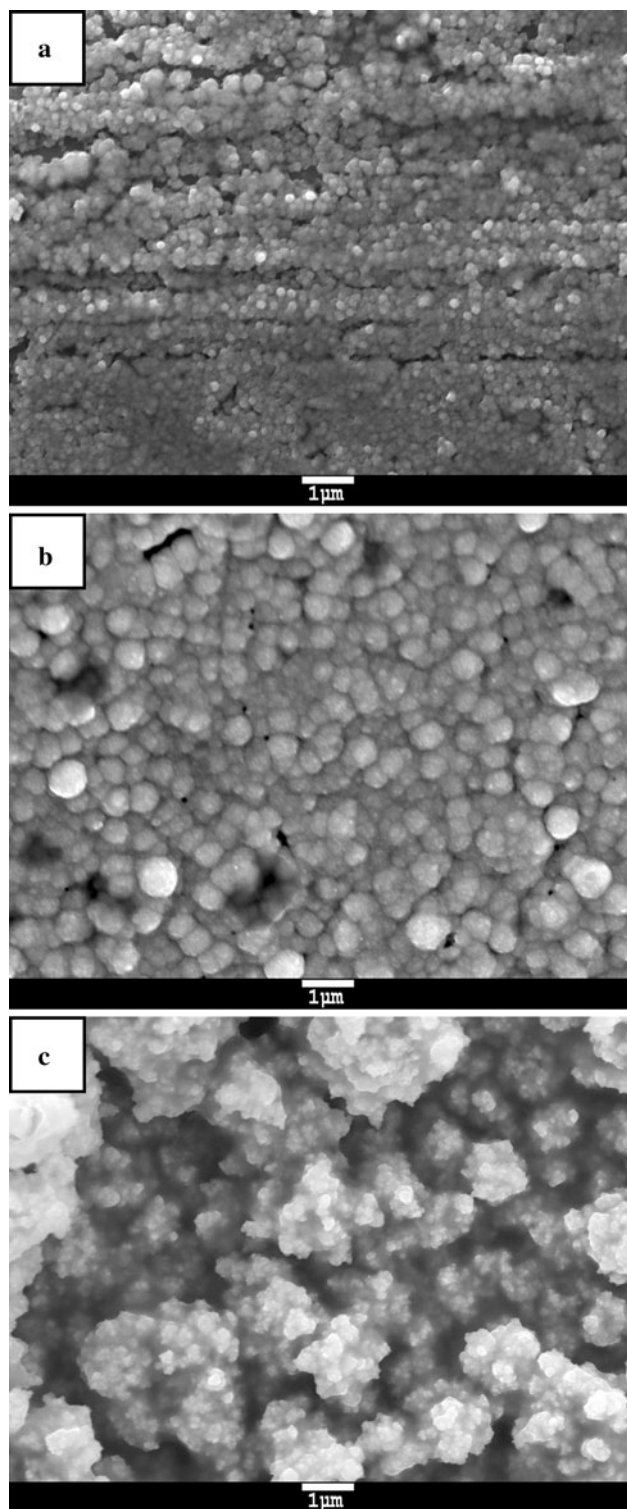


Fig. 5 SEM micrographs of films electrodeposited from 0.1 M CuCl_2 electrolyte at -1.8 V for 900 s at **a** 35, **b** 50 and **c** 85 °C

density limits the size of the grains as there are less room for them to grow. Comparing the films deposited from the CuCl_2 and CuSO_4 solutions, the difference in film morphology was probably due to the difference in the anion of

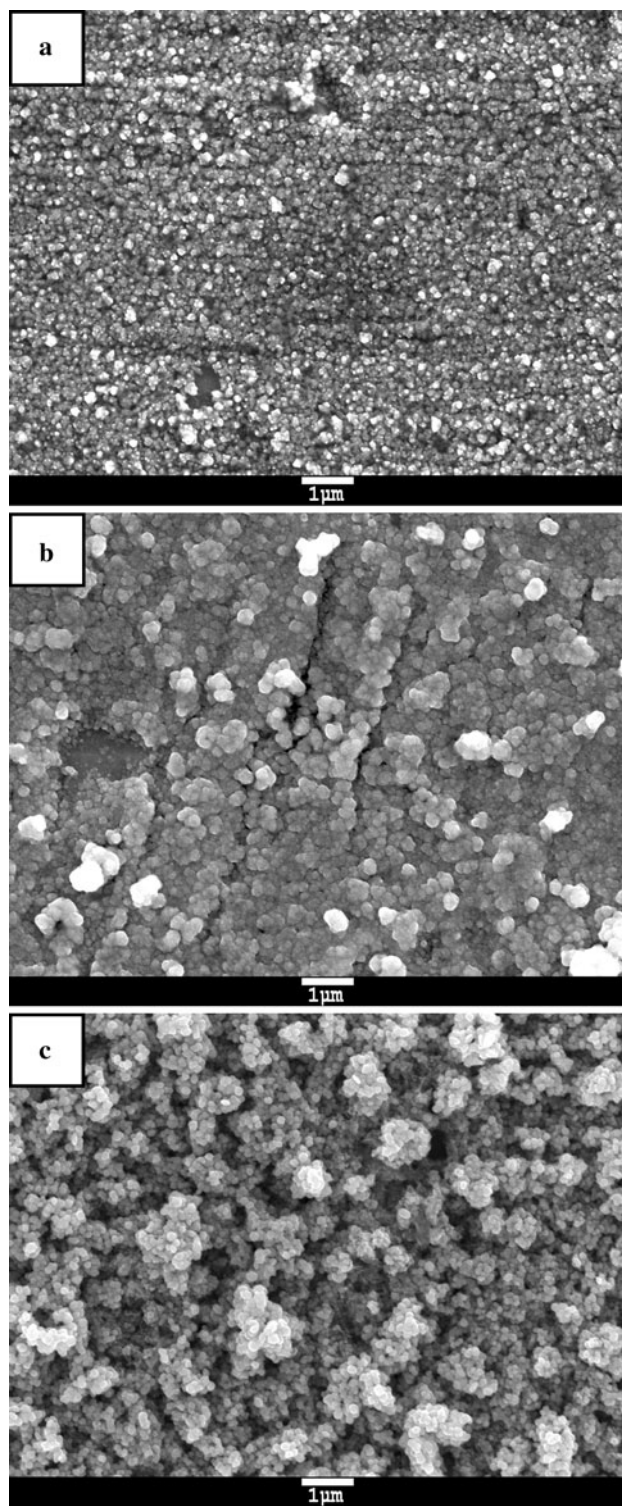


Fig. 6 SEM micrographs of films electrodeposited from 0.1 M CuSO_4 electrolyte at -1.8 V for 900 s at **a** 35, **b** 50 and **c** 85 °C

the salt. The anion of the salts affects how the copper form complexes in solution as well as how the cations and anions in solution form the double-layer structure near the substrate surface. It is well known that the double-layer

structure has a huge impact on the nucleation and growth in ionic liquids and small changes in the double-layer structure can change the size, shape and morphology of the grains [4]. A more detail study into the molecular interactions between the cations and anions in the bulk solution and near the substrate-solution interface is needed in order to get a better understand on the structure and morphology of the films.

The best films are those prepared from CuCl and CuSO₄ electrolytes with -1.8 V applied potential and at 35 °C deposition temperature (Figs. 5a, 6a). Films deposited at 35 °C have smaller particle size, leading to lower surface roughness. Increasing the electrolyte temperature to 50 °C increase the particle size leading to rougher surfaces and for 85 °C the films are still rougher and irregular due to overgrowth. Increasing the applied potential from -1.6 to -1.8 V does not significantly change the morphology of the films deposited from the same electrolytes, but improves the surface coverage for similar deposition parameters.

Comparing our films with those deposited under similar conditions in the literature, the best films obtained were smoother, more uniform and have smaller particle size. Chen et al. [7] were able to obtained crystalline copper on a tungsten substrate from 0.02 M of Cu(I) in EMIM–Cl–BF₄ solution in a glovebox at room temperature. However, their films were much rougher and the particle size was larger (500 nm– 1 μ m) when compared with our film deposited under similar conditions (Fig. 5a), which has an average particle size of 100 nm. The films deposited from the EMIM–Cl–BF₄ solution were very sensitive to the deposition potential, a difference of 0.1 V changes the microstructure of the films [7]. On the contrary, the microstructure of the films in Fig. 5 does not change drastically with the deposition potential. Leong et al. [10] also obtained crystalline copper on a nickel substrate from 0.05 M CuCl in EMIM–DCA in a glovebox at room temperature. Their films were dense and compact, with particle size about 100 nm, that aggregate to form large hemispherical clusters with diameters of 5 μ m. The films obtained in the present work are smoother as no clusters are observed for the film deposited at 35 °C (Fig. 5a), and clusters with diameters of 1 μ m are only observable for the films deposited at 50 °C (Fig. 5b). At a deposition potential of -1.8 V, their films exhibit a cauliflower-like structure which reduced the uniformity and compactness of the films [10]. Similar structures were only observed in the present work for a deposition temperature of 85 °C and long deposition times.

The current efficiency of the CuCl and CuCl₂ solutions were estimated using Faraday's laws of electrolysis. Electrodeposition experiments were carried out on a nickel substrate at a deposition potential of -1.5 V versus a Pt

QRE. For the CuCl solution, the total charges that flow during electrodeposition for a period of 1 h was 0.8335 °C. Assuming that the electrodeposition follows the reaction $\text{Cu}^+ + \text{e}^- = \text{Cu}$, the current efficiency was calculated to be 55% and for the reaction of $\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}$, the current efficiency was calculated to be 109% . For the CuCl₂ solution, the total charges that flow during electrodeposition for a period of 6 h was 6.0539 °C. The current efficiency was calculated to be 43% for the reaction $\text{Cu}^+ + \text{e}^- = \text{Cu}$ and 85% for the reaction $\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}$. These results indicate that for both the CuCl and CuCl₂ solutions, the cathodic deposition may involve a two-electron redox reaction, or the current efficiencies of the reactions are low.

EDX analysis showed that the films consist essentially of copper, with small proportions of oxygen and sulphur, due to traces of electrolyte retained in the film. The chemical composition of the films does not depend on the electrodeposition parameters and on the electrolyte.

X-ray diffractograms of films deposited from CuSO₄ and CuCl solutions are shown in Fig. 7a, b, respectively. The diffractograms present three peaks at 43.4 , 50.5 and 74.2° , which can be indexed as the (111), (200) and (220) peaks of copper. Peaks from the nickel substrate are also observed at 44.5 , 56.8 and 76.4° because the X-ray penetration depth exceeds the film thickness. The average particle size, calculated from the Cu (111) peak full-width at half-maximum using Scherrer's equation was 24 nm for the films obtained from CuSO₄ solutions and 22 nm for the films obtained from CuCl solution. XRD analysis reveals that the films electrodeposited from CuSO₄ and CuCl ionic liquid solutions are polycrystalline with a nanometric grain size.

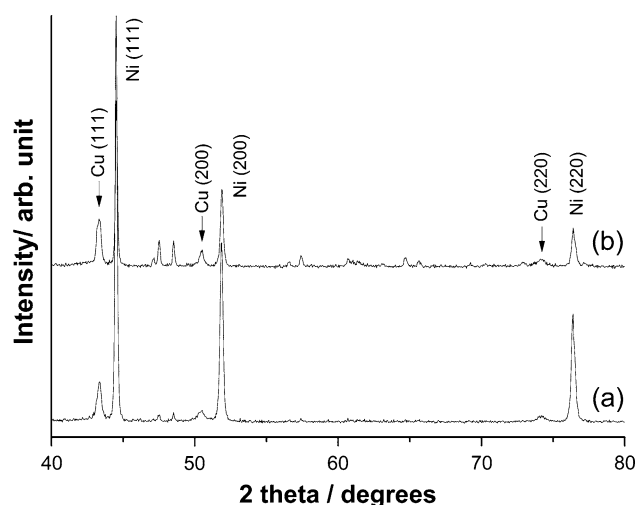


Fig. 7 XRD patterns of copper films electrodeposited at -1.8 V for 900 s from **a** 0.1 M CuSO₄ and **b** 0.1 M CuCl solutions in EMIM–EtSO₄ at 85 °C

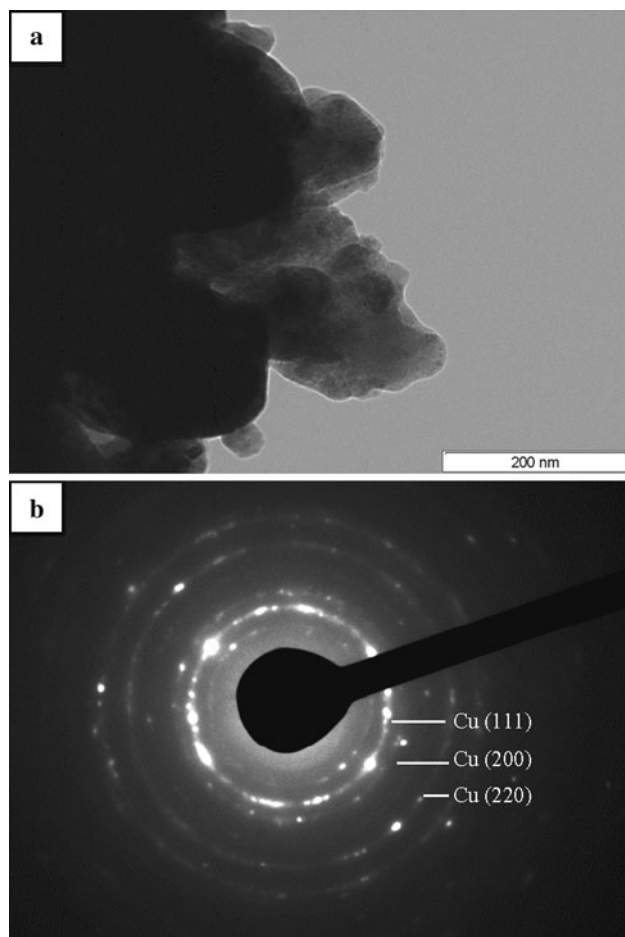


Fig. 8 **a** TEM micrographs of films electrodeposited with -1.8 V for 900 s from 0.1 M CuCl_2 solutions and **b** the corresponding selected area diffraction pattern

TEM analysis was performed on films deposited from a CuCl_2 solution in EMIM- EtSO_4 at 85°C (Fig. 8a). Angular particles with diameters of 200 nm aggregated in large clusters were observed. Electron diffraction patterns of the film (Fig. 8b) consist of rings, typical of a polycrystalline material, which can be indexed as copper (111), (200) and (220) diffractions, in agreement with the XRD results.

4 Conclusions

1. Copper thin films can be electrodeposited from CuCl_2 , CuCl and CuSO_4 solutions in EMIM- EtSO_4 .
2. The films deposited from CuCl_2 solutions consist of large particles and are discontinuous. The best films were obtained for electrolyte temperature of 35 and 50°C , deposition potential of 1.8 V and deposition time of 900 s.
3. The films deposited from CuCl solutions with a deposition time of 900 s are continuous and consist

of globular particles aggregated in clusters. Increasing the deposition time to 1,800 s leads to an overgrowth of the films due to the formation of a cauliflower-like structure.

4. Continuous films could be prepared from CuSO_4 solutions at potentials of -1.6 and -1.8 V for all temperatures and at a potential of -1.2 V for an electrolyte temperature of 85°C . The structure of the films consists of clusters of nanometre size irregular shaped particles.
5. Their continuity and particle size increase when the electrolyte temperature increases from 35 to 85°C for a similar deposition time.
6. Increasing the deposition time from 900 to 1,800 s marginally improves the continuity of the films for the three electrolytes at -1.6 V, although film overgrowth occurs for the CuCl solution.

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